

A Molybdenum(0) Isocyanide Analog of Ru(2,2'-Bipyridine)₃²⁺: Strong Reductant for Photoredox Catalysis

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Abstract: We report on the first homoleptic Mo(0) complex with bidentate isocyanide ligands which exhibits ³MLCT (metal-to-ligand charge transfer) luminescence with quantum yields and lifetimes similar to Ru(bpy)₃²⁺ (bpy = 2,2'-bipyridine). This Mo(0) complex is a very strong photoreductant, manifesting in its capability to reduce acetophenone with essentially diffusion-limited kinetics as shown by time-resolved laser spectroscopy. The application potential of this complex for photoredox catalysis is put in evidence using the example of a rearrangement of an acyl-cyclopropane to a 2,3-dihydrofuran, which is a reaction requiring a reduction potential so negative that even the well-known and strongly reducing Ir(2-phenylpyridine)₃ photosensitizer cannot catalyze it. Thus, our study provides the proof-of-concept for the use of chelating isocyanides to obtain Mo(0) complexes with long-lived ³MLCT excited states which are amenable to unusually challenging photoredox chemistry.

Ru(bpy)₃²⁺ is the prototype of a very large class of metal complexes with long-lived ³MLCT excited states,^[1] comprising many examples based on the precious metals Ru(II),^[2] Os(II),^[3] Re(I),^[4] and Ir(III).^[5] Aside from such d⁶ metal diimines, many Pt(II) and Au(I/III) complexes have favorable luminescence properties,^[6] but emissive complexes made from earth-abundant metals are more difficult to obtain.^[7] Notable exceptions are complexes based on Zn(II) or Cu(I),^[8] but their MLCT excited-states usually undergo strong geometrical distortion,^[9] and nonradiative relaxation to the ground state is rapid. Many of the abovementioned metal complexes have found application for example as triplet harvesters in organic light emitting diodes (OLEDs),^[10] photosensitizers in dye-sensitized solar cells (DSSCs),^[11] or as sensitizers of electron and energy transfer processes in artificial and biological systems.^[12] In recent years, photoredox catalysis has received much attention for organic synthesis,^[13] with Ru(II) and Ir(III) complexes playing a particularly prominent role. Furthermore, Ru(bpy)₃²⁺ and related complexes are now frequently used for the production of solar fuels, for example the light-driven reduction of CO₂ or H₂O.^[14] However, ruthenium is a precious metal with a natural abundance of ~10⁻³ ppm in earth's crust, and even though the luminescence and photoredox properties of Ru(bpy)₃²⁺-type complexes are tunable by ligand variation, there are limitations to this approach. In view of the continued great interest in the abovementioned research areas ranging from synthetic organic

chemistry to materials applications and solar energy conversion, the development of new photosensitizers is highly desirable. The photophysical and photochemical properties of Mo(0) complexes with *monodentate* arylisocyanide ligands were first explored nearly 40 years ago.^[15] Some ³MLCT luminescence was indeed observed, but these complexes become substitutionally labile after photoexcitation, making them unsuitable for most applications.^[15-16] Recently, W(0) complexes with *monodentate* arylisocyanides were found to be strong emitters and photoreductants, but as a 5d metal W(0) is inherently more substitution-inert than the 4d metal Mo(0).^[17] We hypothesized that when using *chelating* arylisocyanides rather than *monodentate* ligands, it might be possible to obtain robust Mo(0) complexes with long-lived ³MLCT excited states and high reducing power.

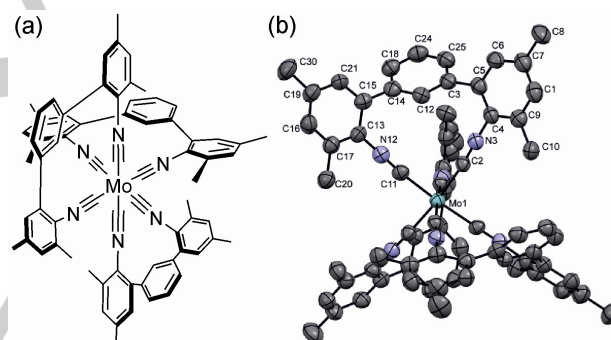


Figure 1. Molecular (a) and crystallographic structure (b) of the Mo(CNAr₃NC)₃ complex; thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Except for a series of older studies,^[18] there has been surprisingly little prior work on chelating isocyanide ligands, particularly with regard to luminescent metal complexes.^[19] We prepared the new 2,2''-diisocyano-3,5,3'',5''-tetramethyl-1,1':3',1''-terphenyl (CNAr₃NC) ligand and reacted it with Mo(THF)₂Cl₄ in presence of Na/Hg to obtain the Mo(CNAr₃NC)₃ complex shown in Fig. 1 (Supporting Information (SI) pages S2-S5). X-ray diffraction on single crystals reveals Mo-C distances of 2.051(5) and 2.056(4) Å, as well as C-Mo-C bite angles between 82.9(2) and 94.2(4)° (SI pages S6-S7). In each ligand there are torsion angles of 51.2(7) and 55.8(7)° between the central benzene ring and the two flanking aryls. Trans-standing isocyanobenzene units are nearly orthogonal to each another. The methyl-substituents help shield the metal center from the environment and thus presumably contribute to the overall stability of the complex. The C≡N stretch frequency in the complex is 1939 cm⁻¹ compared to 2113 cm⁻¹ in the free ligand, indicating substantial π-backbonding (SI page S8).^[20]

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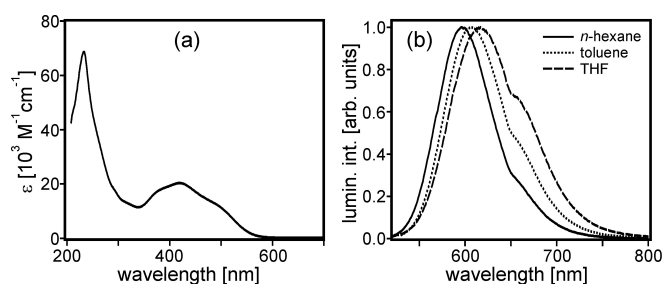


Figure 2. (a) UV-Vis absorption spectrum of $\text{Mo}(\text{CNAr}_3\text{NC})_3$ in THF at 20 °C; (b) luminescence spectra in different solvents at 20 °C ($\lambda_{\text{exc}} = 500$ nm).

In cyclic voltammetry, the $\text{Mo}(0)$ center is oxidized reversibly to $\text{Mo}(\text{I})$ at a potential (E^0) of -0.40 V vs. Fc^+/Fc in THF (SI page S9), in line with a prior report of $\text{Mo}(0)$ complexes with monodentate isocyanide ligands.^[15a]

The UV-Vis absorption spectrum of $\text{Mo}(\text{CNAr}_3\text{NC})_3$ in THF (Fig. 2a) exhibits a broad band between 350 and 560 nm, which is reminiscent of the MLCT absorption of $\text{Ru}(\text{bpy})_3^{2+}$. At shorter wavelengths, there are ligand-based absorptions. The photoluminescence band maximum blue-shifts when going from THF to toluene to *n*-hexane (Fig. 2b), as expected for MLCT emission. The luminescence lifetime (τ) increases from 74 ± 7 (THF) to 166 ± 17 (toluene) to 225 ± 23 ns (*n*-hexane) in deaerated solutions at 20 °C (SI page S11), and in parallel there is an increase of the luminescence quantum yield (ϕ) from 0.6 ± 0.1 to 2.3 ± 0.2 to $4.5 \pm 0.4\%$ (SI page S11). In frozen matrices at 77 K there is a strong rigidochromic effect and emission decays are bi-exponential with lifetimes in the μs regime (SI pages S12–S13). From the 77 K emission spectra we estimate an energy (E_{00}) of 2.2 eV for the emissive $^3\text{MLCT}$ state. The transient absorption spectra of the long-lived $^3\text{MLCT}$ excited state of $\text{Mo}(\text{CNAr}_3\text{NC})_3$ in various solvents are very similar to the spectrum of the $^3\text{MLCT}$ state of $\text{Ru}(\text{bpy})_3^{2+}$ (SI page S10).

Given a potential of -0.40 V vs. Fc^+/Fc in the electronic ground state and an energy (E_{00}) of 2.2 eV for the emissive excited state (see above), a potential of ca. -2.6 V vs. Fc^+/Fc can be expected for oxidation of $\text{Mo}(0)$ to $\text{Mo}(\text{I})$ in the long-lived $^3\text{MLCT}$ state. In order to test this estimate of the excited-state redox potential, the possibility of photoinduced electron transfer with acetophenone (ACP) was explored. The redox potential for the ACP/ACP^- couple in THF is -2.5 V vs. Fc^+/Fc ,^[21] and hence $^3\text{MLCT}$ -excited $\text{Mo}(\text{CNAr}_3\text{NC})_3$ should be thermodynamically competent for the reduction of ACP to ACP^- . Indeed the luminescence of $\text{Mo}(\text{CNAr}_3\text{NC})_3$ in THF is strongly quenched upon addition of ACP (SI page S14), and a Stern-Volmer plot (Fig. 3a) yields a quenching constant of $(3.1 \pm 0.4) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$, which is near the diffusion limit. The transient absorption data in Fig. 3b are fully compatible with the formation of ACP^- and $\text{Mo}(\text{CNAr}_3\text{NC})_3^+$ (see SI page S14–S16 for further details).

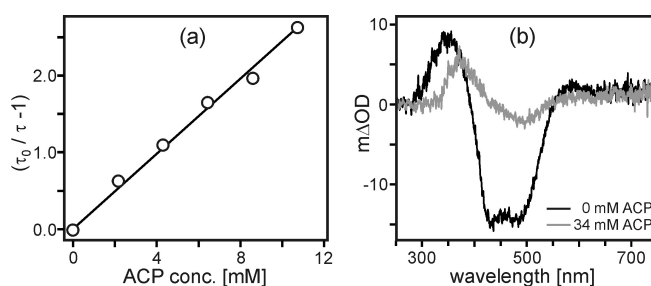
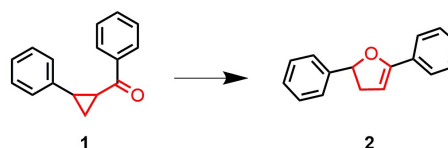


Figure 3. Stern-Volmer plot based on luminescence lifetimes ($\lambda_{\text{det}} = 615$ nm) of $\sim 10^{-5}$ M $\text{Mo}(\text{CNAr}_3\text{NC})_3$ in deaerated THF at 20 °C in presence of increasing concentrations of acetophenone (ACP); (b) Transient absorption of $\sim 10^{-5}$ M $\text{Mo}(\text{CNAr}_3\text{NC})_3$ in absence (black) and presence (grey) of 34 mM ACP. Excitation and detection was as described above. The disappearance of the bleach between 400 and 520 nm is caused by formation of ACP^- radical anion, (ACP^-) see text and SI pages S14–S16.

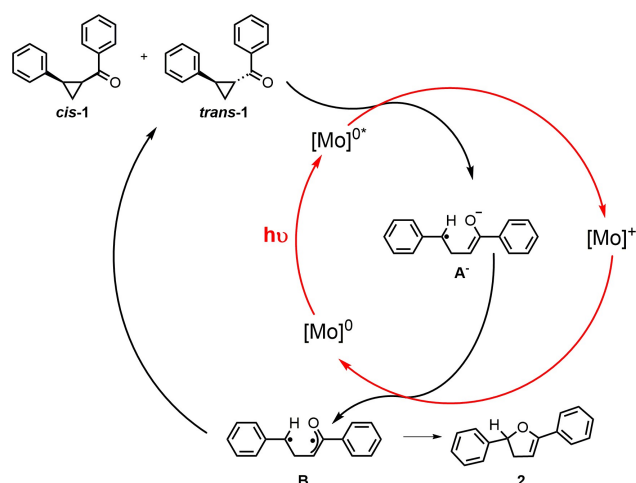
To assess the application potential of $\text{Mo}(\text{CNAr}_3\text{NC})_3$ as a photoredox catalyst, we attempted to perform a rearrangement of an acyl-cyclopropane (**1**) to a 2,3-dihydrofuran (**2**) (Scheme 1), i. e., a reaction which is related to vinylcyclopropane-cyclopentene rearrangements that are important for organic synthesis.^[22] 2,3-Dihydrofurans play key roles as structural elements of biologically active compounds such as for example aflatoxin B₁, and they are considered very useful synthetic intermediates.^[23] We used the reaction in Scheme 1 as a benchmark for the application potential of our complex. Thermally, the conversion of **1** to **2** is very difficult to perform because very harsh conditions or activated groups are necessary.^[24]



Scheme 1. Rearrangement of acyl-cyclopropane (**1**) to 2,3-dihydrofuran (**2**) accomplished in 84% yield by photoirradiation ($\lambda_{\text{exc}} = 455$ nm) of 5% $\text{Mo}(\text{CNAr}_3\text{NC})_3$ in dry benzene- d_6 (TON = 17).

When irradiating a mixture of substrate **1** and 5% $\text{Mo}(\text{CNAr}_3\text{NC})_3$ in dry benzene- d_6 with a blue LED at 455 nm in an evacuated sealed NMR tube, product **2** is formed in 84% yield (at room temperature). When attempting to perform the same reaction with the well-known $\text{Ir}(\text{ppy})_3$ ($\text{ppy} = 2\text{-phenylpyridine}$) photosensitizer, no conversion is observed. We attribute this to the very negative potential required for one-electron reduction of **1** which is necessary to initiate the pericyclic rearrangement via a diradical mechanism. This potential can reasonably be assumed to be similar to that of acetophenone (-2.5 V vs. Fc^+/Fc), and our $\text{Mo}(0)$ complex has sufficient reducing power (-2.6 V vs. Fc^+/Fc) to undergo photoinduced electron transfer with nearly diffusion-limited kinetics (see above). By contrast, the $\text{Ir}(\text{ppy})_3$ photosensitizer has an excited-state reduction potential of only -2.1 V vs. Fc^+/Fc ,^[13c] and therefore is unable to reduce **1** efficiently.

The proposed reaction mechanism for the conversion of **1** to **2** with $\text{Mo}(\text{CNAr}_3\text{NC})_3$ is shown in Scheme 2. Initially only the *trans*-isomer of **1** is present.^[25] Electron transfer between photoexcited $\text{Mo}(\text{CNAr}_3\text{NC})_3$ and *trans*-**1** produces radical intermediate **A**[•] which can be oxidized to diradical **B** by $\text{Mo}(\text{CNAr}_3\text{NC})_3^+$ in the electronic ground state.^[26] **B** can then either undergo intramolecular reaction to form product **2** or it can revert to substrate **1**, thereby producing a mixture of *cis*- and *trans*-isomers. Both diastereomers can then re-enter the catalysis cycle with photoexcited $\text{Mo}(0)$ complex until conversion to **2** is complete. In principle, this can be considered an electron-catalyzed reaction.^[27]



Scheme 2. Proposed reaction mechanism for the conversion of **1** to **2**. $\text{Mo}(0)^*$ denotes the photoexcited $\text{Mo}(\text{CNAr}_3\text{NC})_3$ complex.

Due to the possibility of diradical **B** to undergo forward and backward reactions, the irradiation time to achieve complete conversion to **2** is relatively long, ca. 80 hours. This is evidently an inherent property of the model reaction investigated here and is clearly not a shortcoming of the $\text{Mo}(0)$ sensitizer. We have been able to follow the isomerization of **1** and the conversion to **2** as a function of irradiation time by NMR spectroscopy (SI page S17). The overall yield of **2** is 84%, corresponding to a TON of 17, close to the theoretical limit of 20 at a catalyst loading of 5%. In summary, we have synthesized and characterized the first homoleptic $\text{Mo}(0)$ complex with bidentate isocyanide ligands. Photoexcited $\text{Mo}(\text{CNAr}_3\text{NC})_3$ has roughly 1.3 V more reducing power than $^3\text{MLCT}$ -excited $\text{Ru}(\text{bpy})_3^{2+}$ [1a, 2a, 13c] and it is about 0.5 V more reducing than photoexcited $\text{Ir}(\text{ppy})_3$, [13c, 17a, 28] making it one of the most potent visible-light absorbing photoreductants known to date. The application potential of $\text{Mo}(0)$ complexes with chelating isocyanides for photoredox catalysis has been illustrated in this study using the example of a pericyclic rearrangement which is a very challenging benchmark reaction, because its initiation requires exceptionally strong reductants. The $\text{Mo}(\text{CNAr}_3\text{NC})_3$ complex is able to act as a robust and efficient photoredox sensitizer for this reaction, clearly outperforming the widely used $\text{Ir}(\text{ppy})_3$ complex.

In conclusion, our study provides the proof-of-concept for the use of chelating isocyanides to obtain $\text{Mo}(0)$ complexes with long-lived $^3\text{MLCT}$ excited states which emit visible light and which are amenable to unusually challenging photoredox chemistry.

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Keywords: photochemistry • electron transfer • photocatalysis • luminescence • isocyanide ligands

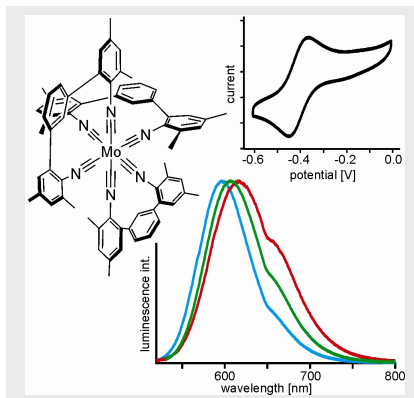
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COMMUNICATION

The first homoleptic Mo(0) complex with chelating isocyanide ligands has been investigated. This chemically robust complex exhibits long-lived $^3\text{MLCT}$ luminescence, and it is a far stronger photoreductant than d^6 metal diimines made from precious metals. Its application potential as a photoredox sensitizer is put in evidence with the rearrangement of an acyl-cyclopropane to a 2,3-dihydrofuran.



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**A Molybdenum(0) Isocyanide Analog
of Ru(2,2'-Bipyridine) $_3^{2+}$: Strong
Reductant for Photoredox Catalysis**